ACCURATE EQUILIBRIUM STRUCTURES FOR *trans*-HEXATRIENE BY THE MIXED ESTIMATION METHOD AND FOR THE THREE ISOMERS OF OCTATETRAENE FROM THEORY; STRUCTURAL CONSEQUENCES OF ELECTRON DELOCALIZATION

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An accurate equilibrium structure of *trans*-hexatriene has been determined by the *mixed estimation* method with rotational constants from 8 deuterium and carbon isotopologues and high-level quantum chemical calculations. In the mixed estimation method bond parameters are fit concurrently to moments of inertia of various isotopologues and to theoretical bond parameters, each data set carrying appropriate uncertainties. The accuracy of this structure is 0.001 Å and 0.1°. Structures of similar accuracy have been computed for the cis,cis, trans,trans, and cis,trans isomers of octatetraene at the CCSD(T) level with a basis set of wCVQZ(ae) quality adjusted in accord with the experience gained with *trans*-hexatriene. The structures are compared with butadiene and with *cis*-hexatriene to show how increasing the length of the chain in polyenes leads to increased blurring of the difference between single and double bonds in the carbon chain. In *trans*-hexatriene r("C_1=C_2") = 1.339 Å and r("C_3=C_4") = 1.346 Å compared to 1.338 Å for the "double" bond in butadiene; r("C_2–C_3") = 1.449 Å compared to 1.454 Å for the "single" bond in butadiene. "Double" bonds increase in length; "single" bonds decrease in length.